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Characterization of Treatment Residues from Hazardous Waste Treatment, Storage, and Disposal Facilities

Metcalf and Eddy, Inc., Wakefield, MA

Prepared for

Environmental Protection Agency, Cincinnati, OH

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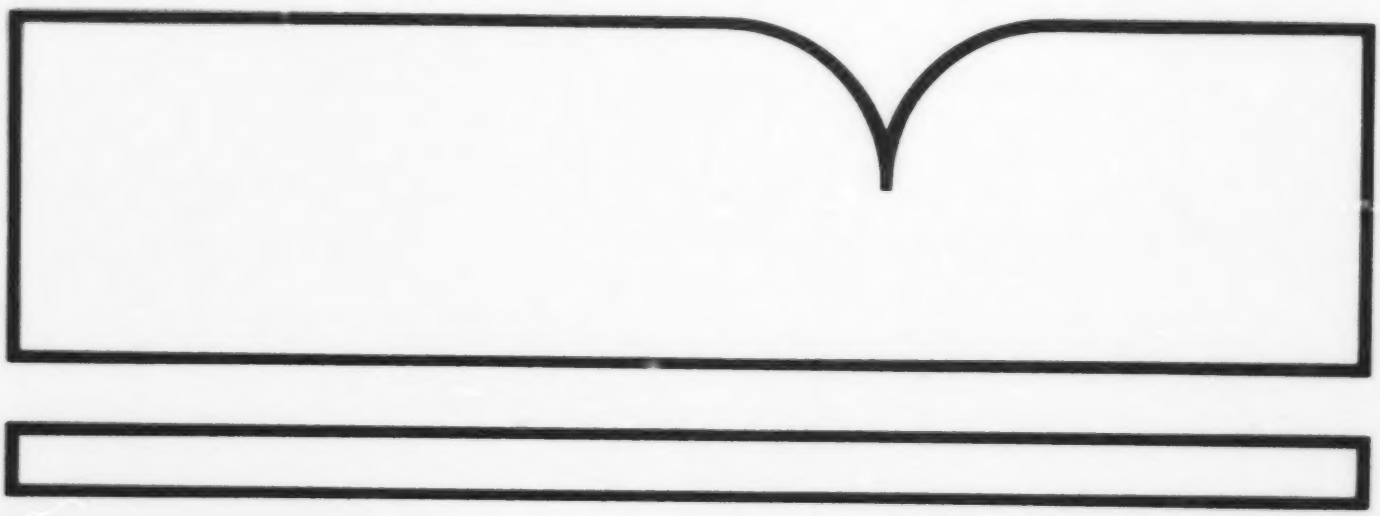

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16. ABSTRACT

To implement the Congessionally mandated land disposal prohibitions of the 1984 amendments to the Resource Conservation and Recovery Act (RCRA), EPA must determine whether adequate treatment technologies exist, what wastes can be treated and how effectively, what residues and environmental discharges are produced, and what the associated costs are.

As part of the program to develop this information, characterization of treatment residues from technologies treating or destroying wastes that have been listed for priority action were determined. The primary focus of this study was to characterize residues resulting from treatment of solvent (F001-F005) wastes and metal-bearing (inorganic compounds on the California list) hazardous wastes.

A diversity of waste types, process configuration, and operating procedures were examined. These are discussed and data are presented on waste and treatment residue characteristics, including data from a second generation leaching procedure, the Toxicity Characteristic Leaching Procedure (TCLP) and its predecessor, the EP Toxicity Characteristic.

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CHARACTERIZATION OF TREATMENT RESIDUES FROM HAZARDOUS WASTE TREATMENT, STORAGE, AND DISPOSAL FACILITIES

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INTRODUCTION

The RCRA Hazardous and Solid Waste Amendments of 1984 mandate that a ban on land disposal of hazardous wastes be considered. EPA is required to evaluate alternative technologies for each waste category and to establish treatment standards for banned wastes based on the lowest level achieved by a best demonstrated available technology (BDAT). As part of the program to develop this information, field evaluation of alternative technologies for treating or destroying wastes that have been listed for priority action were conducted The primary focus of this study was to evaluate the treatability of metal-bearing and solvent (F001-F005) wastes. This paper presents information on existing technologies being applied to the treatment of these wastes, the effectiveness of these processes, and the environmental impacts of these processes in terms of residues and emissions.

FACILITY A

Process Description

Facility A is a commercial off-site treatment facility accepting aqueous wastes generated by the electroplating

any remaining dissolved metals. The sulfide polishing reagent was a by-product scrubber solution from the production of a sulfurized ester (RCRA waste code D003). The contents of the reactor are pumped to one of two precoat vacuum filters for solids separation. Perlite, a volcanic ash, is currently used as a precoat although diatomaceous earth has been used in the past. The filtrate from the precoat filter is discharged to the municipal sewer system. The solids scraped from the filter are conveyed to segregated bulk containers. Samples from each container are subjected to the 24-hour EP toxicity test to ensure it is nonhazardous prior to transport to a final disposal site.

Waste Characterization

Eleven separate batches of liquid waste (each approximately 6,000 to 10,000 gallons in volume) were completely processed during the sampling episode. Of the eleven batches, three required pretreatment for cyanide oxidation, six required hexavalent chromium reduction and all eleven were treated by chemical precipitation and vacuum filtration. Five of the eleven batches were similar in nature, the primary waste requiring treatment being a sludge slurry from a common chrome and brass electroplating generator. Similar proportions of a lime slurry, waste chromic acid, ferrous-iron acid, waste nitric acid, sulfide containing waste, and rinsewaters (or dilute wastewater from floor drains) were blended with the primary waste. Analytical data for each waste stream and of the composite mixture are

presented in Table 2 for one of these batch cycles (which was comparable to the other four batches treated).

The electroplating waste did not contain cyanide, therefore, initial cyanide pretreatment was not necessary. The waste contained greater than 100 mg/kg of lead, zinc, and chromium. The small volume of waste chromic acid added to the primary waste contained over 75,000 mg/kg of hexavalent chromium. The waste ferrous acid used as the reducing acid contained high levels of nickel and chromium as did the nitric acid used for pH adjustment. The sump wastewater had concentrations of four metals greater than 100 mg/kg, while the sulfide waste generally had metal concentrations below 10 mg/kg. The reaction tank composite had levels of chromium exceeding 2,000 mg/kg and levels of cadmium, nickel, and zinc in the 100 mg/kg range. An interesting observation was the presence of several volatile organic compounds in the 0.5 ppm range.

Residue Characterization

Analytical data characterizing the filter cake and filtrate are presented in Table 3 The low levels of metals found in the filtrate indicates that both the precipitation and filtration process performed well.

As previously discussed, several volatile organic compounds were found to be present in the reaction tank composite sample. The levels of organics found in the filtrate (<0.01 mg/l) and filter cake (between 0.130 mg/l and 0.470 mg/l) indicates that

industry, as well as other metal finishing operations. Table 1 summarizes the types of waste streams treated during the sample episode including their SIC code and RCRA waste code.

The liquid treatment process, depicted in Figure 1, entails four basic processes: cyanide oxidation, hexavalent chromium reduction, metals precipitation, and solids separation. The cyanide oxidation process uses a waste sodium hypochlorite solution to oxidize cyanide in a single-stage batch reactor. The waste used during the sampling episode was a scrubber solution from the production of chlorinated chemicals (RCRA Waste Code D003). Typically, few incoming wastes necessitate treatment for cyanide.

Hexavalent chromium is reduced to trivalent chromium in a single-stage batch reactor, using iron-bearing (ferrous) waste acid as the reducing agent. The waste used during the sampling episode was a waste picking acid from the metal processing industry (RCRA Waste Code K062). The chromium reduction is accomplished under alkaline conditions in order to minimize corrosion of equipment and eliminate the potential emission of by-product gases (e.g. NO_2, Cl_2) that could be generated under acidic reaction conditions. Upon successful reduction of the hexavalent chromium, the waste is then precipitated similar to all other treatment batches.

The chemical precipitation process entails addition of both a lime slurry, to initially precipitate the heavy metals as their insoluble hydroxides, and a soluble sulfide waste to precipitate

these compounds were apparently partitioned to the sludge as a result of the treatment process. However, organic levels found in the TCLP extract from the filter cake were within the regulatory limits of the recently promulgated land disposal ban.

Although metal concentrations found in the filter cake are high (ex. chromium 16,300 mg/l), the metals are bond sufficiently to pass the EP toxicity test.

FACILITY B

Facility Description

Facility B is a chemical manufacturing plant owned and operated by a major chemical company. Both solid and liquid hazardous organic wastes generated on-site and at several other company plants are incinerated at Facility B. Solid wastes and sludges are received in drums and typically include paint sludges, chlorinated hydrocarbons, coke solids, vacuum filter solids, waste filter elements and polymeric tar. Liquid wastes, transportated on-site by bulk tanker truck, commonly include waste organic solutions, waste solvents, tank farm nitrates and chloroprene catalyst sludge.

The incineration system, depicted in Figure 2, includes both a rotary kiln incinerator and single-stage liquid injection incinerator. The liquid injection incinerator burns exclusively liquid wastes, which are predominantly generated from the manufacturing operations on site. The rotary kiln incinerator typically burns the same liquid wastes, in addition to a variety

of solid wastes. Both incinerators use natural gas as an auxiliary fuel. The total system thermal input rating is 40 million BTU/hr.

The rotary kiln is followed by a natural gas-fired afterburner designed to further oxidize gases exiting the kiln. Normal operating temperatures for the rotary kiln are 1200-1400°F; afterburner temperatures are 100 to 150°F higher. Average solid residence times in the kiln are between 40 and 60 minutes, and the kiln rotation is between 0.10 and 0.20 revolutions per minute. Ash is discharged continuously from the kiln to an ash sluice.

The liquid incinerator is air atomized and care is taken to prevent plugging of the feed lines. Tanks and feed lines are flushed with toluene between burning incompatible liquid wastes. Normal operating temperature for the liquid incinerator ranges from 1400 to 1600°F. Ash is removed from the liquid kiln about four times per year.

Each of the two incinerators is followed by a water quench and a cyclone. The quench serves to cool effluent gases, while the cyclone acts to remove entrained particulates and droplets prior to scrubbing. Gases exiting the two cyclones combine to form a single exhaust stream. The combined gas stream then passes through a three-stage packed tower absorption (scrubber) system for removal of particulates and HCl.

There are two waste streams generated by incineration at facility B: Ash residue and scrubber wastewater. Ash residue is typically allowed to accumulate in the ash sluice and slurry tank for about four weeks. The rotary kiln is shut down approximately once a month for ash removal. Ash is landfilled on-site.

Waste Characterization

During the week-long sampling program, Facility B incinerated the contents of one 20,000 gallon liquid blend tank along with 183 drums representing five different types of solid waste. The solid waste types were: chlorinated hydrocarbon cake from dichlorobutene synthesis, polymeric tar, filtered organo-metallic waste solids from adiponitrile area, adiponitrile spent filter cartridges, and scrap paint solids. Table 4 presents a summary of the physical and chemical characteristics of each waste.

Toluene was the major volatile organic reported in the liquid waste and in several of the solid wastes. A number of semivolatile compounds were reported in one or more of the waste samples. Copper and nickel are the two metals present in the greatest concentrations in the liquid waste and they are reported at significant levels in each of the solid wastes as well. Solid waste #5, the scrap paint solids, exhibits the highest metals concentrations with high levels of lead, chromium and zinc, three common pigment metals.

The fuel value of the solid wastes ranged from 5,866 BTU/lb for the polymeric tar to 12,000 BTU/lb for the scrap paint solids. The liquid waste had a fuel value of 11,926 BTU/lb, a water content of 17 weight percent and a halide content of 14.24 weight percent.

Residue Characterization

Neither volatile nor semivolatile organic compounds were found in either the ash samples themselves or the TCLP extracts. Compositional analysis of the ash indicated measurable concentrations of eight toxic metals, with copper (4,600 mg/kg), nickel (4,200 mg/kg) and zinc (1,160 mg/kg) reported at the highest concentrations. The metal levels found in the TCLP extract, although quite high for copper, nickel and zinc, were within the land disposal regulations. The ash had a total solids content of about 81 weight percent and a specific gravity of about 1.94. The ash contained nearly 18 weigh percent silica. Table 5 summarizes the analytical data for the ash residue.

The scrubber wastewater was very acidic, with a pH <1. Four toxic metals-copper, lead, nickel and zinc are present at concentrations greater than 25 mg/l. Volatile and semi-volatile organic compounds were not detected in the scrubber wastewater. Analytical results are presented in Table 6.

CONCLUSIONS

The treatment train utilized at Facility A successfully removed the metal compounds from the water environment. The metals were removed to below the pretreatment limits imposed by the local municipality. Moreover, the sludge sample extracts were within the threshold limits for metals and organics of the land disposal regulations.

Evaluation of the data from Facility B indicates that significant levels of toxic metals are present in waste solvents and organic process wastes destined for incineration. Since metals are not destroyed by incineration, they tend to concentrate in the treatment residues - ash and scrubber wastewater. Properly designed and operated incineration systems should achieve virtually complete destruction of organic compounds. This appears to be the case at Facility B, where detectable levels of volatile or semivolatile organics were not found in either the ash of the scrubber wastewater.

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Table 1. Facility A - Industrial Sources of Liquid Wastes

Industry Category	Industry (SIC Code)	Process	RCRA waste code
Fabricated metal products	Refurbishing of used field artillery (3471)	Chrome & brass electroplating	F006
Fabricated metal products	Electroplating (3471)	Chrome electroplating	D002
Fabricated metal products	Manufacture of toasters, toaster ovens, and coffee makers (3634)	Nickel and chrome electroplating	F006
Fabricated metal products	Reclamation of tin from scrap metal (3341)	Etching, electroplating	D002
Chemical manufacturing and processing	Manufacture of glass perfume bottles (3621)	Etching	D002
Fabricated metal products	Manufacture of aluminum windows, doors, sashes and mouldings (3442)	Conversion coating of aluminum	F019
Fabricated metal products	Manufacture of semiconductors and electrical connectors (3678, 3643)	Nickel, chrome and gold electroplating	F006
Fabricated metal products	Manufacture of aluminum bottle caps (3466)	Cleaning	D002
Fabricated metal products	Surface finishing of sheet steel-anodizing, painting and etching (3316)	Cleaning	K062

D002 - Corrosive waste that has a pH less than or equal to 2 or greater than or equal to 12.5.

F006 - Wastewater treatment sludges from electroplating operations except from the following processes: (1) sulfuric acid anodizing of aluminum; (2) tin plating on carbon steel; (3) zinc plating (segregated basis) on carbon steel; (4) aluminum or zinc - aluminum plating on carbon steel; (5) cleaning/stripping associated with tin, zinc and aluminum plating on carbon steel; and (6) chemical etching and milling of aluminum.

F019 - Wastewater treatment sludges from the chemical conversion coating of aluminum.

K062 - Spent pickle liquor from steel finishing operations.

Table 2. Facility A-Waste Characterization

PARAMETER	Electroplating Waste	Wastewater Neutral Sump	Waste Ferrous Acid	Waste Chromic Acid	Waste Nitric Acid	Sulfide Containing Waste	Reaction Tank Composite
VOLUME (gallons)	4770	1974	1200	100	140	5	10,193(b)
VOLATILE ORGANIC COMPOUND (mg/kg)							
1,1-dichloroethane	NS	NS	NS	NS	NS	NS	.340
1,1,1-trichloroethane	NS	NS	NS	NS	NS	NS	.220
Trichloroethane	NS	NS	NS	NS	NS	NS	.99
1,1,2,2-tetrachloroethylene	NS	NS	NS	NS	NS	NS	.074
Toluene	NS	NS	NS	NS	NS	NS	.140
Ethylbenzene	NS	NS	NS	NS	NS	NS	.200
METALS (mg/kg)							
Arsenic	<1	<1	<1	<1	3	<1	<1
Barium	<10	<10	<10	<10	<10	<10	<10
Cadmium	19	<5	<5	7	<5	<5	10
Chromium	760	470	7,000	103,800	1,800	7	2311
Lead	125	250	<10	60	<10	12	108
Mercury	<1	<1	<1	<1	<10	<1	<1
Selenium	<10	<10	<10	<10	<1	<10	<10
Silver	<2	<2	<2	<2	<2	<2	<2
Hexavalent chromium	0.016	0.148	I	78,400	I	0.016	0.1
Copper	36	40	306	3,500	865	<3	72
Nickel	14	355	2,600	40	3,200	<3	426
Zinc	190	410	<2	250	<2	9	171

(b) - In addition to the components listed includes 1445 gallons of lime slurry and 559 gallons of water washes.
NS - Not sampled
I - Analytical color interference

Table 3. Facility A-Residual Characterization

PARAMETER	Filtered Effluent	Filter cake	EP Toxity	TCLP	Land Disposal Regulations
VOLATILE ORGANIC COMPOUND (mg/l)					
1,1-dichloroethane	<0.01	0.340*	NA	0.022	None
1,1,1-trichloroethane	<0.01	0.470*	NA	0.017	30
Trichloroethylene	<0.01	0.130*	NA	<0.01	0.07
1,1,2,2-tetrachloroethlene	<0.01	0.150*	NA	<0.01	None
Toluene	<0.01	0.230*	NA	0.017	14.4
Ethylbenzene	<0.01	0.390*	NA	0.017	None
METALS (mg/l)					
Arsenic	< 0.1*	1*	<0.05	<0.01	<5.0
Barrium	<1*	30*	0.02	0.18	<100
Cadmium	< 0.5	20*	0.0008	<0.02	1.0
Chromium	0.12	16,300*	<0.01	<0.05	5.0
Lead	<0.01	375*	0.08	0.10	5.0
Mercury	0.1	<1*	<0.002	0.002	0.2
Selenium	<1*	<10*	<0.01	<0.01	1.0
Silver	< 0.2*	<2*	0.01	<0.02	5.0
Hexavalent chromium	0.121	I	<0.005	0.01	None
Copper	0.16	330*	0.05	NS	None
Nickel	0.40	1,700*	0.10	NS	None
Zinc	0.115	375*	0.01	NS	None

NA - Not applicable
NS - Not sampled
I - Analytical color interference
* - Units are in mg/kg

Table 4. Facility B-Waste Characterization*

PARAMETER	Liquid Blend	Solid #1 Chlorinated Hydrocarbon Coke	Solid #2 Polymeric Tar	Solid #3 Filtered Organo-Metallic Waste Solids	Solid #4 Spent Filter Cartridges	Solid #5 Scrap Paint Solids
VOLATILE ORGANICS (ppb)						
Carbon disulfide	37,000	<62,000	<62,000	<62,000	<62,000	<62,000
Benzene	47,300	<62,000	<62,000	<62,000	52,000	<62,000
Toluene	340,000,000	10,200,000	<62,000	4,900,000	850	11,700,000
Ethylbenzene	80,300	<62,000	<62,000	72,000	<62,000	4,600,000
Styrene	181,700	<62,000	<62,000	59,000	<62,000	<62,000
Xylenes	47,900	<62,000	<62,000	340,000	<62,000	20,200
4-methyl - 2-pentanone	<10,000	<120,000	<120,000	<120,000	<120,000	250,000
SEMIVOLATILE ORGANICS (ppb)						
Benzyl alcohol	1,300,000	<7,500	<60,000	<190,000	<110,000	<7,500
1,2 dichlorobenzene	1,867,000	<7,500	<60,000	357,000	<110,000	<7,500
N-nitrosodiphenylamine	3,233,000	<7,500	<60,000	497,000	<110,000	<7,500
Naphthalene	<50,000	<7,500	<60,000	490,000	<110,000	60,300
2-methylnaphthalene	<50,000	<7,500	<60,000	2,900,000	<110,000	<7,500
Acenaphthene	<50,000	<7,500	<60,000	70,700	<110,000	<7,500
Phenol	<50,000	<7,500	<60,000	<190,000	184,000	<7,500
Di-n-butyl phthalate	<50,000	<7,500	<60,000	<190,000	<110,000	22,300
Butyl benzyl phthalate	<50,000	<7,500	<60,000	<190,000	<110,000	217,000
TOXIC METALS (ppm)						
Antimony	<1	<1	4	116	<1	12
Arsenic	<0.1	<0.1	<0.1	0.21	<0.1	<0.1
Barium	<1	<1	<1	21	4.5	29
Beryllium	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Cadmium	<0.5	<0.5	<0.5	1.3	<0.5	<0.5

Table 4. (Continued). Facility B-Waste Characterization*

PARAMETER	Liquid Blend	Solid #1 Chlorinated Hydrocarbon Coke	Solid #2 Polymeric Tar	Solid #3 Filtered Organo-Metallic Waste Solids	Solid #4 Spent Filter Cartridges	Solid #5 Scrap Paint Solids
Chromium-hexavalent	0.23	.09	0.26	SI	0.015	0.085
Chromium - total	2.2	2.1	0.83	67	10	992
Copper	68	5,700	85	74	1,013	347
Lead	1.7	<1	<1	30	<1	3,470
Mercury	<0.1	<0.1	<0.1	0.9	0.4	<0.1
Nickel	227	91	1.2	500	1,200	39
Selenium	<1	<1	<1	<1	<1	<1
Silver	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Thallium	<1	<1	<1	<1	<1	<1
Zinc	4.8	1.8	1.0	195	60.5	1,670
OTHER ANALYSES						
Wt% Carbon	54.96	48.00	43.12	29.09	IS	50.44
Wt% Hydrogen	8.46	3.61	6.70	6.69	IS	6.45
Wt% Water	17.16	33.91	7.45	27.61	IS	0.52
Wt% Organic Halide	14.24	NS	NS	NS	NS	NS
Wt% Silica	<0.01	0.77	0.44	15.35	6.99	2.81
Sp. Gravity	0.9576	1.0548	1.2325	1.1313	1.0431	1.1191
Total Solids (mg/kg)	73,000	565,600	659,800	626,033	132,550	604,200
BTU/lb.	11,926	6,243	7,944	5,866	IS	12,000

NS - Not Sampled
SI - Sample Interference
IS - Insufficient sample
* Each value represents the average of three grab samples.

Table 5. Facility B - Ash Characterization*

PARAMATER	Compositional (mg/kg)	TCLP Extract (mg/l)	Regulatory Level (mg/l)
TOXIC METALS			
Antimony	14.5	0.03	None
Arsenic	<0.1	0.004	5.0
Barium	75	0.39	100.0
Beryllium	<0.2	0.002	None
Cadmium	<0.5	0.01	1.0
Hexavalent Chromium	0.05	<10	None
Total Chromium	361	0.085	5.0
Copper	4,600	96	None
Lead	340	0.56	5.0
Mercury	1.6	0.004	0.2
Nickel	4,200	34	None
Selenium	<1	<0.05	1.0
Silver	<0.2	<0.005	5.0
Thallium	<1	<0.001	None
Zinc	1,160	25	None
OTHER ANALYSES			
Silica (wt%)	17.77	-	-
Total Solids (mg/kg)	811,000	-	-
Specific Gravity	1.9363	-	-

* Each Value Represents the Average of Six Grab Samples

Table 6. Facility B-Scrubber Wastewater Characterization*

PARAMETER	Scrubber Wastewater
Toxic Metals (mg/kg)	
Antimony	<1
Arsenic	<0.1
Barium	2
Beryllium	<0.2
Cadmium	<0.5
Chromium-hex	0.2
Chromium-total	1.5
Copper	241
Lead	106
Mercury	<0.1
Nickel	27
Selenium	<1
Silver	<0.2
Thallium	<1
Zinc	363
Other Analyses	
Total Solids (mg/kg)	3867
Total Dissolved Solids (mg/kg)	3500
Total Suspended Solids (mg/kg)	67
Total Organic Halide (wt%)	0.08
Total Chlorine (wt%)	1.59
Specific Gravity (g/mL)	0.9936
pH	0.7

*Each value represents the average of 3 grab samples.

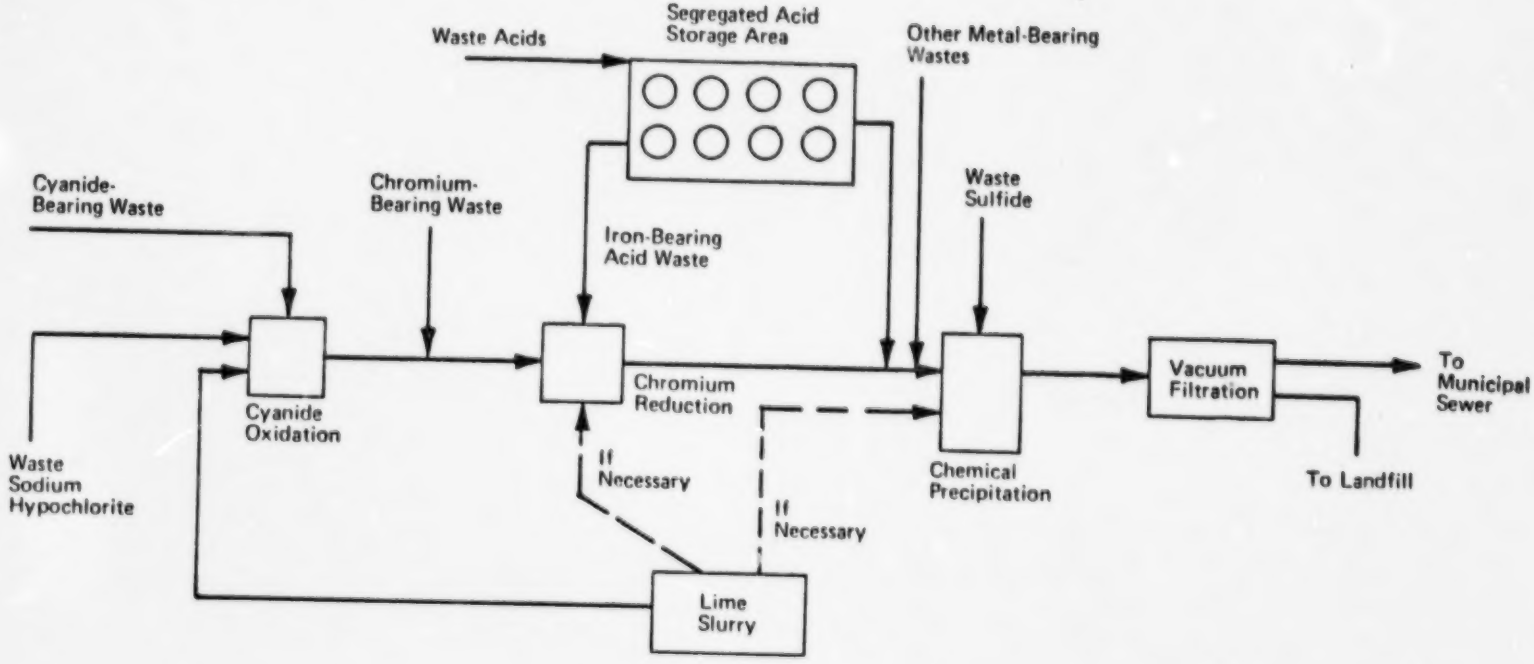

Figure 1. Waste Treatment Process-Facility A

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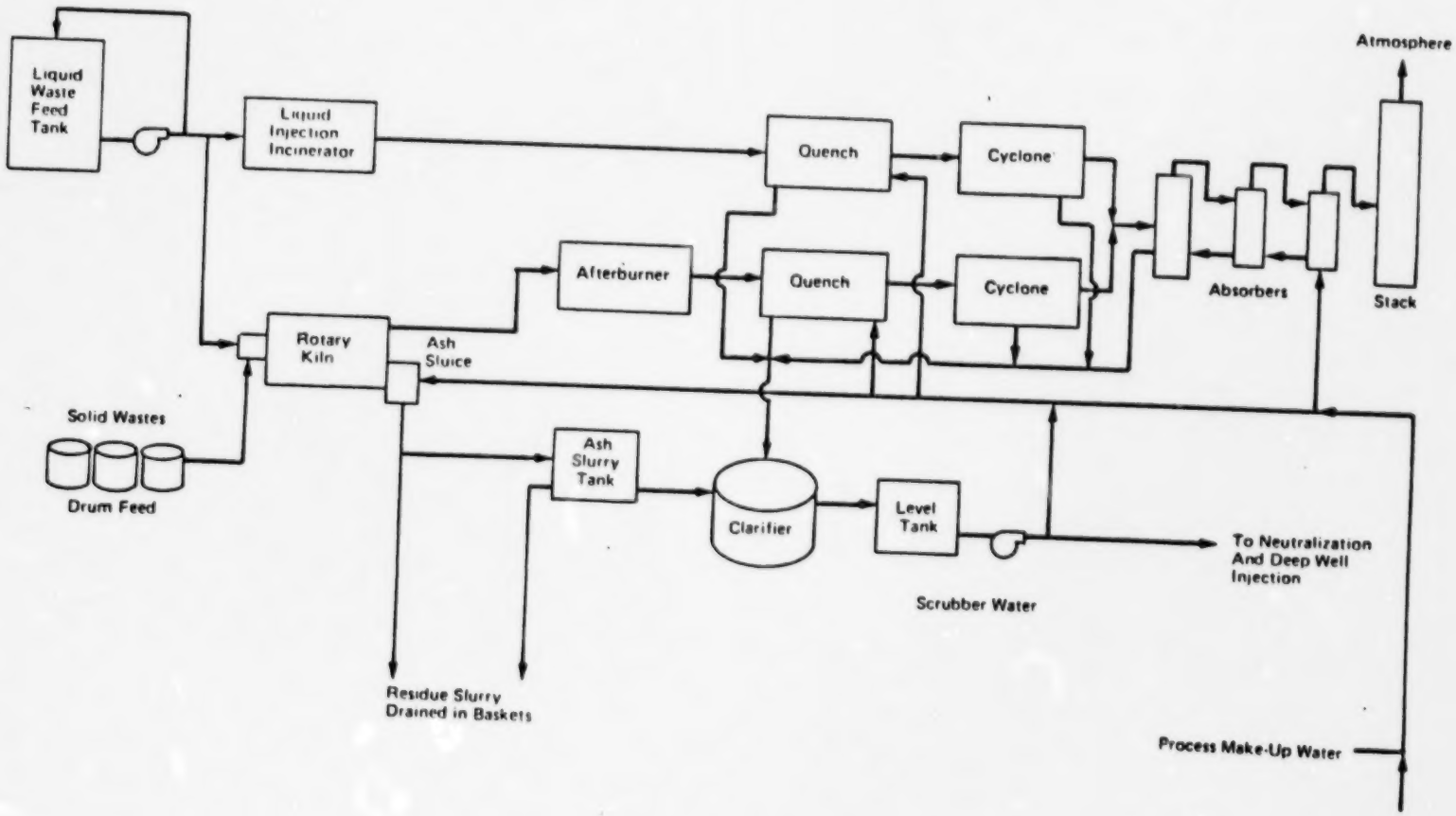

Figure 2. Facility B process flow diagram